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IN SITU PLASMA PROCESS TO REMOVE FLUORINE RESIDUES
FROM THE INTERIOR SURFACES OF A CVD REACTOR

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BACKGROUND

In the fabrication of semiconductor integrated
10   circuits on silicon wafers, chemical vapor deposition
(CVD) or plasma-enhanced chemical vapor deposition
(PECVD) forms dielectric or metallic films on the wafers
at relatively low temperatures, such as 400°C. During
the deposition process, the films are deposited not only
15   on the wafers but also on the interior surface of CVD or
PECVD reactor/chamber, in which the deposition process
occurs. The deposition residue on the interior surface
of the chamber can be a contamination source that may
reduce the yield of subsequent deposition processes in
20   the reactor. Thus, the residue is periodically removed.

The periodic removal of the deposition residue is
performed by a chamber cleaning that uses a fluorine-
based plasma. The reaction between the plasma and the
deposition residue forms volatile products, which are
25   evacuated from the chamber. For example, the fluorine-
based chamber cleaning may be carried out after every
fifty wafers have been processed. However, the fluorine-
based plasma leaves sorbable contaminants and residues on
the interior surface of the chamber. Normally, these
30   contaminants and residues are removed only during primary

maintenance, where the chamber is vented to the
atmosphere and the interior surface of the chamber is
physically scrubbed. Primary maintenance is performed
far less frequently, e.g., after every 10,000 wafers.

5   The fluorine residue tenaciously adheres to the
interior reactor surfaces of the CVD chamber and is
extremely difficult to remove. Further, the fluorine
residue can generate significant localized concentrations
of HF when the chamber is opened to the atmosphere for

10   the primary maintenance. Accordingly, the fluorine
residue needs to be removed between the primary
maintenance procedures, and a number of methods for
removing fluorine residue have been developed.

The methods include purging the chamber with a

15   hydrogen-containing or reducing gas, dissociating a
reducing gas in a remote plasma source and then
introducing it into the chamber, generating an H_2 plasma
in the chamber followed by purging the chamber with a
dilute SiH_4 mixture, generating a plasma of an inert gas

20   in the chamber, and coating the interior surfaces of the
CVD chamber with an oxide layer to trap the residual
fluorine.

U.S. Patent No. 5,647,953, which is incorporated
herein by reference in its entirety, discloses a method

25   for removing oxide and fluorine residues in a plasma
process chamber. The method energizes fluorine
containing gas into plasma and, using the plasma, removes
oxide residue from interior surfaces of a CVD chamber.
Then the interior surfaces are coated with silicon

30   dioxide in order to trap fluorine impurities from the
prior fluorine plasma-cleaning step. The silicon dioxide
coating often leaves some of the fluorine impurities

without the coating. Finally, a hydrogen-containing gas
(SiH_4, Si_2H_6, H_2, and/or H_2O) is introduced into the
chamber in non-plasma state to remove the fluorine
impurities uncoated in the prior coating step. This
5   final step may be done as a purge, or the chamber may be
pressurized and then evacuated.

U.S. Patent No. 5,935,340, which is incorporated
herein by reference in its entirety, describes a method
for removing residues from the interior surfaces of a CVD
10 chamber. This method dissociates a fluorine containing
gas such as NF_3 in a remote plasma source and then
introduces the dissociated gas into the chamber to clean
residues from the interior chamber surfaces. NH_3, H_2,
and/or SiH_4, are then introduced into the chamber to
15 remove fluorine residue remaining from the prior step.
In the removal of the fluorine residue, in order to cause
a heat-induced chemical reaction between fluorine and
NH_3, H_2, and/or SiH_4 without in situ plasma excitation, a
heater in the chamber maintains a temperature greater
20 than 550 °C and less than about 600 °C. NH_3, H_2, and/or
SiH_4 may first be dissociated in a remote plasma source
before being introduced into the chamber. The clean
reactants produced in the heat-induced chemical reaction,
such as HF, SiF_4, and/or an ammonium fluoride compound,
25 are then evacuated from the chamber.

U.S. Patent No. 5,824,375, which is incorporated
herein by reference in its entirety, describes a method
for removing sorbable contaminants from the interior
surfaces of a chemical vapor deposition plasma reactor.
30 This method includes cleaning the reactor with a plasma
of a cleaning gas having a fluorine source that leaves
sorbable contaminants and removing the sorbable

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contaminants with a plasma of a plasma of an inert gas, such as He. Then, a seasoning film is deposited on the interior reactor surfaces to block or retard remaining contaminants.

5   U.S. Patent No. 5,129,958, which is incorporated herein by reference in its entirety, discloses a method of treating the fluorine residues in a CVD chamber left from a prior fluorine plasma cleaning step. This method contacts the fluorine residues with one or more reducing

10   gases, such as SiH_4, NH_3, H2, PH_3, B_2H_6, and/or AsH_3, to form one or more reaction products. The flow rate of the reducing gases is between 100 and 500 sccm (standard cubic centimeters per minute). While flowing the reducing gases, the CVD chamber is maintained at a

15   temperature of 250 to 500°C and a pressure of 10^{-3} to 100 Torr. The reducing gases react with the fluorine residues to form one or more gaseous and/or solid reaction products. Optionally at least a portion of the reaction products is removed from the CVD chamber.

20   U.S. Patent No. 5,207,836, which is incorporated herein by reference in its entirety, describes a procedure for a removal of tungsten or tungsten silicide deposits from the susceptor of a vacuum deposition chamber by fluorine plasma cleaning and a removal of

25   fluorine residues introduced by the plasma cleaning step. In this method, the tungsten-based residues are first removed by flowing a gaseous source of fluorine, such as SF_6, NF_3, C_2F_6, and/or CF_4, into the chamber and igniting a plasma. Then, in order to remove the fluorine residue,

30   a gaseous source of hydrogen, such as H_2, B_2H_6, PH_3, 1-2 carbon hydrocarbons, are flowed into the chamber at a rate of approximately 100 to 500 sccm, and a plasma is

ignited. While the gaseous source of hydrogen is flowed,
the pressure in the chamber is maintained at a pressure
from about 0.2 to 1 Torr and the susceptor is maintained
at a temperature from about 150 to 525 °C.

5   U.S. Patent No. 5,326,723, which is incorporated
herein by reference in its entirety, discloses a method
for cleaning a chemical vapor deposition chamber
following tungsten deposition. After the tungsten
deposition, an in-situ cleaning with an NF_3 based plasma
10 is used to remove tungsten residue from the chamber.
This cleaning step produces fluoride-containing by-
products. In the next step, an in-situ cleaning with an
H_2 based plasma is performed in the chamber. This plasma
leaves hydrogen fluoride (HF), hydrogen (H), and fluorine
15 (F) species in the chamber. Finally the chamber is
purged with a mixture of SiH_4, N_2, and Ar at a pressure
between 0.1 to 5 Torr, wherein the silane is between 1
and 2% of the mixture. The result of the last step is to
replace a portion of the fluorine containing compounds on
20 the interior chamber surfaces with SiF_4 and H_2. These
gases (SiF_4 and H_2) and by-products are subsequently
evacuated from the chamber.

        U.S. Patent No. 6,020,035, which is incorporated
herein by reference in its entirety, describes a method
25 for reducing the level of fluorine absorbed in films
deposited on substrates in a PECVD (Plasma Enhanced CVD)
chamber after a fluorine based chamber clean. In this
method, a fluorine containing gas is introduced into the
chamber to remove the deposition residue from the
30 interior chamber surfaces. This cleaning process leaves
a residue including fluorine atoms on the interior
chamber surfaces. In the next step, a plasma of a

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process gas containing silicon and oxygen is used to
deposit a silicon oxide film on the interior chamber
surfaces. The plasma uses both low frequency (< 2 MHz)
and high frequency (> 2 MHz) RF power sources, with the
5   low frequency power source providing a power density
greater than 3.10 W/cm^2. The high power level of the low
frequency RF signal increases the ion bombardment and
favors the formation of stable SiF bonds between silicon
and fluorine atoms. This leads to fewer loosely bonded
10   fluorine atoms being incorporated into the layer and
fewer fluorine atoms outgassing in subsequent process
steps.

Although the prior art described above removes
fluorine residue from CVD chambers, the effectiveness of
15   fluorine residue removal process and the speed of the
process still need improvement.

SUMMARY

The present invention is directed to a method for
20   removing fluorine residues from a process chamber used in
fabricating a semiconductor wafer. After chemical vapor
deposition (CVD) or plasma-enhanced chemical vapor
deposition (PECVD) for depositing silicon or tungsten
containing films on a semiconductor substrate in a CVD
25   chamber, a fluorine-based plasma is often introduced into
the CVD chamber to remove the silicon or tungsten
containing deposits on the interior surface of the CVD
chamber. This fluorine-based plasma cleaning leaves
fluorine residues, which can be removed by the method of
30   the present invention.

The method includes: supplying an oxygen-containing
gas and a hydrogen-containing gas into a CVD chamber;

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producing a plasma of a mixture of the oxygen-containing gas and the hydrogen-containing gas, so that the plasma reacts with the fluorine residue, exothermically generating water; and evacuating from the CVD chamber a

5 product of the reaction between the plasma and the fluorine residue. For the hydrogen-containing gas, NH_3 is often used, and for the oxygen-containing gas, N_2O, O_2, or air is used. Exemplary mixtures of the oxygen-containing and the hydrogen-containing gases include 70

10 mol % N_2O/NH_3, 50 mol % N_2O/NH_3, and 52 mol % O_2/NH_3. An inert gas, such as He, Ne, Ar, or Kr, can be optionally supplied into the chamber to stabilize the plasma.

The fluorine residue removing method according to the present invention can utilize the source gases, such

15 as N_2O, O_2, and NH_3, already plumbed to a CVD chamber for standard deposition processes. That is, no additional gases or modifications of the existing gas manifold are necessary. N_2O is preferred to O_2 as the oxygen-containing source gas, because N_2O produces a relatively

20 electronegative discharge that is very stable and diffuse.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow chart illustrating a fluorine

25 residue removing method in accordance with the present invention.

Figure 2 is a graph illustrating relative volumetric quantities of HF removed in fluorine residue removing methods in accordance with the present invention.

30 Figure 3 is a graph illustrating relative volumetric quantities of H_2O produced in the fluorine residue removing methods of Figure 2.

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Figure 4 is a graph illustrating relative volumetric quantities of H_2 produced in the fluorine residue removing methods of Figure 2.

Figure 5 is a graph illustrating relative volumetric quantities of HF removed in another fluorine residue removing method in accordance with the present invention.

Figure 6 is a graph illustrating relative volumetric quantities of H_2O produced in the fluorine residue removing method of Figure 5.

Figure 7 is a graph illustrating relative volumetric quantities of H_2 produced in the fluorine residue removing method of Figure 5.
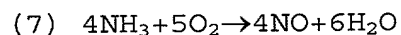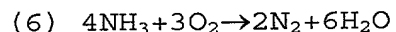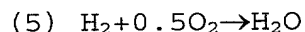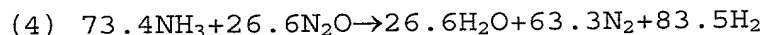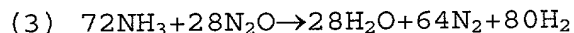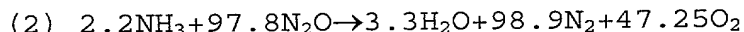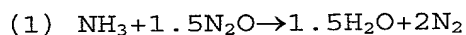
DETAILED DESCRIPTION

The present invention is directed to a method for removing fluorine residues from the interior surfaces of a CVD chamber prior to primary maintenance. The method eliminates fluorine residues adhering to the interior reactor surfaces of the CVD chamber and prevents the formation of localized concentration of HF when the chamber is opened to atmosphere for primary maintenance.

The method generates a plasma and creates a very aggressive chemical environment that rapidly reacts with residual fluorine. The plasma exothermically generates water in the chamber to purge the fluorine residues. Any CVD chamber that has a supply of a hydrogen-containing gas, such as NH_3, and an supply of an oxygen-containing gas, such as O_2, N_2O, or air, can employ the method according to the present invention to remove the fluorine residues in the CVD chamber. In order to implement the method, the CVD chamber must be equipped with a RF power source. For instance, the method can be immediately

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implemented in a Concept Two Sequel Express™ reactor, available from Novellus Systems, Inc., of San Jose, California.

5   In a method according to the present invention, a hydrogen-containing gas, such as NH_3, and an oxygen-containing gas, such as O_2 or N_2O, are fed into a CVD chamber and ignited to form a plasma. N_2O is preferred for the oxygen containing gas. An inert gas, such as He, Ne, Ar, or Kr, can be introduced into the chamber to

10 stabilize the plasma discharge. The plasma exothermically forms H_2O in the CVD chamber. The exemplary exothermic H_2O formations are illustrated below as equations (1) to (7). The components of the reactions are at gaseous state during the reactions.

15

(1) $NH_3 + 1.5N_2O \rightarrow 1.5H_2O + 2N_2$

(2) $2.2NH_3 + 97.8N_2O \rightarrow 3.3H_2O + 98.9N_2 + 47.25O_2$

(3) $72NH_3 + 28N_2O \rightarrow 28H_2O + 64N_2 + 80H_2$

(4) $73.4NH_3 + 26.6N_2O \rightarrow 26.6H_2O + 63.3N_2 + 83.5H_2$

20 (5) $H_2 + 0.5O_2 \rightarrow H_2O$

(6) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

(7) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

The exothermic generation of H_2O in the presence of

25 H, OH, and O radicals and ions creates a very aggressive chemical environment that rapidly reacts with the fluorine residues in the CVD chamber. The heat produced from the exothermic H_2O generation increases the reaction rate between the plasma and the fluorine residue. It is

30 believed that this aggressive chemical environment results not only from the exothermic formation of H_2O,

but also from the presence of an energetic ion flux moving toward the surface, which results in an ion-enhanced chemical reaction. In addition, the plasma produces extremely reactive radicals and ions, such as OH

5   radicals and ions. These radicals and ions, which are coordinately and electronically unsaturated, can rapidly react with the fluorine residue. Although the exact nature of the fluorine residue is not known, the residue rapidly reacts to form HF and other fluorine-containing

10   products, such as ammonium fluorides, when NH_3 is employed as the hydrogen-containing source gas. The HF and other volatile fluorine products are then evacuated from the chamber prior to opening it for primary maintenance.

15   In the method of the present invention, the combined effect of the plasma-produced reactants, a flux of energetic ions on the interior surface of CVD chamber, and the exothermic formation of H_2O results in the aggressive environment that significantly enhances the

20   removal rate of fluorine residue.

Figure 1 illustrates a flow chart of a fluorine residue removing method in accordance with the present invention. After chemical vapor deposition (CVD) or plasma-enhanced chemical vapor deposition (PECVD) for

25   depositing silicon or tungsten containing films on a semiconductor substrate in a CVD chamber, a fluorine-based plasma is introduced into the CVD chamber to remove the silicon or tungsten containing deposits on the interior surface of the CVD chamber. The fluorine-based

30   plasma cleaning, which can be performed in-situ or remote, uses a fluorine containing gas such as CF_4, C_2F_6, C_3F_8, C_4F_8, C_4F_8O, SF_6, NF_3, or F_2 for the plasma source,

and optionally adds an oxygen containing gas such as O_2 and/or a carrier gas such Ar, Ne, Kr, or He.   The plasma cleaning time depends on the thickness of the deposits in the CVD chamber.

5   After the fluorine-based plasma cleaning, fluorine residues, which may be the combinations of the residual gases (SiF_4, HF, F_2, COF_2, etc.) from the fluorine-based chamber deposition cleaning, remain in the chamber. Thus, as shown in Figure 1, in-situ fluorine residue

10   cleaning (or removing) is performed to remove the fluorine residues.   In this embodiment of the invention, a hydrogen-containing gas, NH_3, and an oxygen-containing gas, N_2O, are supplied into the CVD chamber so as to form 70 mol % N_2O/NH_3 gas mixture, and the mixture is ignited

15   to form an in-situ 13.56 MHz plasma.   Exemplary process conditions of the fluorine residue cleaning are described below with reference to Figures 2 to 7.

        Then, volatile fluorine products, primarily HF, that result from the reaction between the cleaning plasma and

20   the fluorine residues are evacuated from the chamber. The H_2O generated from the exothermic reactions discussed above is also evacuated with the volatile fluorine products from the chamber

        Referring to Figures 2 to 4, the effectiveness of a

25   fluorine residue cleaning method, which uses an N_2O/NH_3 mixture to produce an N_2O/NH_3 plasma, is explained. Experiments, which used 70 mol % N_2O/NH_3, 50 mol % N_2O/NH_3, and 100 mol % NH_3, respectively, to produce a fluorine residue cleaning plasma, were performed in a

30   Concept Two Sequel Express™ chamber, available from Novellus Systems, Inc., of San Jose, California.   In the

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experiments, a CVD and a subsequent in-situ fluorine-
based plasma cleaning using an NF_3/He mixture were
commonly performed before the fluorine residue cleanings.
The flow rate of NH_3 was 1,500 sccm (standard cubic

5   centimeter per minute), and the flow rate of N_2O was
varied from 0 to 3,500 sccm. He gas was also introduced
at a flow rate of 100 sccm into the chamber as an
internal standard for the analysis of the Quadrupole Mass
Spectrometer (QMS) data. A high frequency (13.56 MHz) RF

10 power of 3,000 W was applied to the chamber to produce
the plasmas, and the pressure of the chamber was 2 Torr.
The emissions during the fluorine residue cleanings were
characterized with a Quadrupole Mass Spectrometer (QMS)
mounted directly to the chamber.

15   Figure 2 illustrates relative volumetric quantities
of HF removed in the fluorine residue cleanings which
used 70 mol % N_2O/NH_3, 50 mol % N_2O/NH_3, and 100 mol % NH_3
plasmas, respectively. The plasmas of N_2O/NH_3 mixtures
resulted in more effective HF removal than the 100 mol %

20 NH_3 plasma. For example, the volumetric HF emission by
the 70 mol % N_2O/NH_3 plasma was the largest and
approximately 316% greater than the volumetric HF
emission of the 100 mol % NH_3 plasma. In addition, the
plasma of 70 mol % N_2O/NH_3 was more effective in removing

25 HF than the plasma of 50 mol % N_2O/NH_3.

        Figures 3 and 4 respectively illustrate the relative
quantities of H_2O and H_2 produced during the experiments
of Figure 1, that is, during the discharges of the 70 mol
% N_2O/NH_3, 50 mol % N_2O/NH_3, and 100 mol % NH_3 plasmas.

30 The N_2O/NH_3 plasmas exothermically produced appreciable
quantities of H_2O, while the NH_3 plasma produced almost
no H_2O. The plasma of 70 mol % N_2O/NH_3 produced more H_2O

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than the plasma of 50 mol % N_2O/NH_3 did. In contrast,

the 100 mol % NH_3 plasma generated more H_2 molecules than

the N_2O/NH_3 plasmas did. The plasma of 50 mol % N_2O/NH_3

produced more H_2 than the plasma of 70 mol % N_2O/NH_3 did.

5   Accordingly, Figures 3 and 4 show that the effectiveness

of the fluorine residue cleaning process is related to

the quantity of H_2O, not H_2, produced during the process.

Referring to Figures 5 to 7, the effectiveness of a

fluorine residue cleaning method which uses O_2/NH_3

10   mixture to produce O_2/NH_3 plasma is explained.

Experiments, which used 52 mol % O_2/NH_3 and 100 mol % NH_3,

respectively, to produce a fluorine residue cleaning

plasma, were performed in a Novellus Systems 200 mm

Sequel Express chamber. As in the experiments of Figures

15   2 to 4, a CVD and a subsequent in-situ fluorine-based

plasma cleaning using an NF_3/He mixture were commonly

performed before the fluorine residue cleanings using a

52 mol % O_2/NH_3 plasma and a 100 mol % NH_3 plasma. The

flow of NH_3 was 2,000 sccm, and the flow rate of O_2 was

20   varied from 0 to 2,170 sccm. He gas was also introduced

at a flow rate of 100 sccm into the chamber as an

internal standard for the analysis of the QMS data. A

high frequency (13.56 MHz) RF power of 2,000 W was

applied to the chamber to produce the plasmas, and the

25   pressure of the chamber was 3 Torr.

Figure 5 illustrates the relative volumetric

quantities of HF removed in the fluorine residue

cleanings which used the 52 mol % O_2/NH_3 plasma and the

100 mol % NH_3 plasma, respectively. The 52 mol % O_2/NH_3

30   plasma resulted in more effective HF removal than the 100

mol % NH_3 plasma. The volumetric HF emission by the 52

mol % O_2/NH_3 plasma was approximately 295% greater than the volumetric HF emission of the 100 mol % NH_3 plasma.

Figures 6 and 7, respectively, illustrate the relative quantities of H_2O and H_2 produced during the
5   experiments of Figure 5, that is, during the discharges of the 52 mol % O_2/NH_3 and the 100 mol % NH_3 plasmas.   The O_2/NH_3 plasma exothermically produced appreciable quantities of H_2O, while the NH_3 plasma produced almost no H_2O.   In contrast, the 100 mol % NH_3 plasma generated
10   more H_2 molecules than the O_2/NH_3 plasmas did. Accordingly, Figures 6 and 7 show the same relationship between the effectiveness of the fluorine residue cleaning process and the quantity of H_2O produced during the process as the relationship shown by Figures 3 and 4.
15   The fluorine residue removing method according to the present invention can utilize the source gases, such as N_2O, O_2, and NH_3, already plumbed to a CVD chamber for standard deposition process.   That is, no additional gases or modifications of the existing gas manifold are
20   necessary. N_2O is preferred as the oxygen-containing source gas, because N_2O produces a relatively electronegative discharge that is very stable and diffuse.   For CVD chambers that do not have an oxygen-containing source gas available, mixtures of air and a
25   hydrogen-containing source gas may be employed to produce plasma.

Finally, when the fluorine residue removing method according to the present invention uses N_2O as the oxygen-containing gas and NH_3 as the nitrogen-containing
30   gas, care must be taken to insure that the gas mixture is diluted since N_2O and NH_3 are incompatible gases. Adequate N_2 purge may accomplish the dilution before the

gas mixture enters the compressive stage of the mechanical backing pump. Similar consideration must be given to other gas mixtures employed.

5 For instance, the flammability triangle of $N_2/N_2O/NH_3$ mixtures shows that the LEL (Low Explosive Limit) depends upon the extent of nitrogen dilution. To stay at or below the LEL, $70\%N_2O/NH_3$ gas mixture must be diluted with N_2 until N_2 constitutes at least 85% of the gas mixture. In the absence of the N_2 dilution, the hazards 10 associated with this gas mixture increase exponentially. To ensure an appropriate safety margin, a given flow rate of $70\%N_2O/NH_3$ gas mixture must be diluted with N_2 until N_2 constitutes a minimum of 90% of the gas mixture before the gas mixture enters the compressive stage of the 15 mechanical backing pump.

In summary, the method of the present invention significantly enhances the removal rate of fluorine residue, compared to previously known methods, by creating the aggressive environment for fluorine residue 20 removal reaction. This enhancement is the result of the combined effect of the plasma-produced reactants, a flux of energetic ions on the interior surface of CVD chamber, and the exothermic formation of H_2O.

The invention has been described using exemplary 25 embodiments. However, it is to be understood that the scope of the invention is not limited to the disclosed embodiments. On the contrary, it is intended to cover various modifications and similar arrangements. The scope of the claims, therefore, should be accorded to the 30 broadest interpretation so as to encompass all such modifications and similar arrangements.